EFFECT OF SALT ON COFORMATION OF LOW MOLECULAR WEIGHT SODIUM POLYSTYRENE SULFONATE

A Dissertation submitted for partial fulfilment

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By

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DECLARATION

I hereby declare that the work presented in this thesis wascarried out by me at Department of Physics, National Institute of Technology, Rourkela. I further declare that to best of my knowledge the experimental work presented here has not formed the basis for the award of any degree, diploma, or similar title of any university or institution.

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CERTIFICATE

This is to certify that the thesis entitled "**EFFECT OF SALT ON COFORMATION OF LOW MOLECULAR WEIGHT OF SODIUM POLYSTYRENE SULFONATE**" submitted by **Miss Subhashree Pradhan**in partial fulfillment of the requirements for the award of Master of Science in Physics at the National Institute of Technology, Rourkela is an authentic experimental work carried out by him under my supervision.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/Institute for the award of any degree or diploma.

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ABSTRACT

The dimensional changes of the sodium sulfonated polystyrene of low molecular weight 70kDa with the variation of the salt (NaCl) were studied using dynamic light scattering and viscosity measurements. It was found from the viscosity measurements that the sample viscosity decreased on the increasing the added electrolyte concentration from 0M to 2M. From the dynamic light scattering measurements we found the hydrodynamic radius of the polyelectrolyte decreased from ~ 33 nm at zero salt concentration to ~ 6nm at the highest electrolyte concentration of 2M.

CHAPTER – I

INTRODUCTION:

Polyelectrolytes are the materials having polymeric backbone with electrolytic groups covalently attached to it. Polyelectrolytes in polar solvents such as water, dissociate leaving charges on polymer chains and releasing counter ions in solution. Some of the common examples of polyelectrolytes are sodium sulfonated polystyrene, polyacrylic acid, DNA, RNA, and Poly – L – Lysine. Because of the electrostatic interactions between charges on the backbone of the polymer, the polyelectrolytes gives rise to rich behaviour in solution as compared to neutral polymers.

Polyelectrolytes can be classified as natural or synthetic polyelectrolytes based on their origin. Examples of natural polyelectrolytes are Nucleic acids, Poly – L – Lysine, Poly (L-glutamic acid), Polypeptides, Glycosaminoglycans, etc and those of synthetic polyelectrolytes are sodium sulfonated polystyrene (NaPSS), Poly Acrylic Acid (PAA), Poly methacrylic acid and their salts. Also the polyelectrolytes can be classified as cationic or anionic polyelectrolytes depending on whether they bear positive or negative charge respectively on their backbone. Examples of anionic polyelectrolytes are Nucleic acids, Poly (L-glutamic acid), sodium sulfonated polystyrene and those of cationic polyelectrolytes are Poly – L – Lysine and Polyallylamine hydrochloride. Further, the polyelectrolytes can be classified as strong or weak polyelectrolytes based on their degree of dissociation in solution. Polyelectrolytes which remain fully charged over a wide range of solution pH are called strong polyelectrolytes, where as in the case of weak polyelectrolytes the charge density on the polymer backbone can be varied significantly by tuning the solution pH. Sodium sulfonated polystyrene is a strong polyelectrolyte as oppose to polyacrylic acid which is a weak polyelectrolyte.

As described above polyelectrolyte dissociates in the polar solvent into polyions and counterions. Due to the equal and neighbouring charges on the backbone of the polymer, there is an electrostatic repulsion which straightens the chain. At high charge densities with low salt concentration, the polyelectrolytes assume a rigid rod like conformation. With increase in salt concentration the charges on the polymer backbone are screened and their strength decreases exponentially with the distance between charges. At high salt concentration the polyelectrolyte chains assume structure similar to that of the neutral polymers in a good solvent.

Literature Survey

Many theoretical and experimental researches on the polyelectrolytes have been done by different groups.

E.Dubois and F.Boué and group studied the conformation of sodium sulfonated polystyrene (NaPSS) and perdeutearted polystyrene in presence of multivalent cations using Small Angle Neutron Scattering (SANS) and found NaPSS remains wormlike at lower ionic strength. However at higher ionic strength it assumes a coil structure. With the increase in the charge of the cations at higher ionic strength the polyelectrolyte chains becomes thicker and more expanded [1].

Eiji Kanemaru, Ken Terao, Yo Nakamura et al, performed light scattering, small angle X- ray scattering and viscometry measurements on sodium sulfonated polystyrene (NaPSS) . It has been investigated that the side chains of sodium poly(styrene sulfonate) have Kuhn length 7.5 times than that of the polystyrene in toluene. This stiffening might be due to the electrostatic repulsion between the charged groups of polyelectrolyte brush [2].

Ben Yean and D. Thirumalai, developed a theory to predict the conformation of polyelectrolytes under different solvent quality and salt concentration. While the polyelectrolyte attains a swollen state in a good solvent it transforms itself to a globular state in a poor solvent. A similar transformation is observed for the polyelectrolyte conformation on increasing the salt concentration [6].

Khan et al studied the conformational changes in DNA molecules using both Monte Carlo simulations and fluorescence microscopy. They predicted the presence of regions with strong electrostatic interactions. Moreover they found that the conformation of polyelectrolyte did not exhibit significant variation within the temperature range of $5 - 65℃$ [5].

Jeng- Shiung Jan et al investigated the variation in the viscosity of NaPSS solutions in dilute regimes under the effect of salt. They found the behaviour of the solutions varied significantly in presence of different trivalent salts. They found that in the presence of indium chloride ($InCl_3$) the NaPSS collapses at lower salt concentration but re-expands at intermediate salt concentration. However on further increasing the salt concentration the polyelectrolytes exhibited a secondary collapse [7].

Motivation

Polyelectrolytes have been extensively studied for their biological as well as non-biological relevance. Most of the biopolymers known till date are polyelectrolyte in nature

with common examples being deoxyribonucleic acid (the genetic material in cells), ribonucleic acid, and proteins. Understanding the functioning of these requires a thorough knowledge of their nature. The polyelectrolytes have been well exploited for their charged nature in different fields such as drug delivery, pharmaceuticals, biomedical applications, cosmetic industries, mineral processing, as thickeners, dispersants, and flavour while other uses include battery applications, paper making, paints, waste water treatment. The sequential assembly of oppositely charged polyelectrolytes in an alternating layer by layer fashion has recently become a useful tool for controlling fabrication of organic thin film and modification of surface in aqueous media, the use of weak polyelectrolyte allow flexibility in the film architecture. Recently it has been found that the use of weak polyelectrolyte in thin film is highly advantageous due to the ability to control the layer thickness by tuning the ionization fraction of polyions. Again, when the polyelectrolytes are covalently attached to a surface, the polymer chain shows a strongly extended conformation in pure water due to the repulsion between neighbouring chains and also the repulsion between two monomers. As a result of which polymer brush is formed which are use to driven highly reversible and multistage cantilever actuation**.** Its various properties like flexible and tuneable conformation and its various applications have paved the path for me to work on it.

CHAPTER – II

EXPERIMENTAL TECHNIQUES

2.1 Dynamic Light Scattering

As the name suggests the dynamic light scattering (DLS) probes the dynamic properties of the polymer solutions and gels like relaxation time, diffusion coefficient and hydrodynamic radius.

Interaction of electromagnetic wave with matter induces dipole moments within the material. This dipole oscillates with the electric field of electromagnetic wave and each oscillating dipole gives rise to secondary radiation which is known as scattered wave. In a solution the molecules are in random motion due to the collision with solvent molecules. These random motions of molecules are commonly known as the Brownian motion. Because of the random motion the induced dipoles change their position continuously as a result of which the scattered intensity fluctuates with time. The Brownian motion of the particles leads Doppler's shift in frequency (wavelength) due to which the wavelength of the scattered light is slightly shifted around the incident wavelength. DLS is therefore known as Quasielastic scattering. The fluctuation in the intensity of the scattered beam gives the information about the diffusion coefficient of the particles which in turn is related to the hydrodynamic radius of the diffusing particles through Stokes – Einstein relation. Hence, the particle size can be determined by analyzing the scattered light.

The rate at which the spontaneous fluctuation in the electric field decays to equilibrium has direct dependence on dynamics of the molecules. The normalized field-field autocorrelation function $g_1(\tau)$ is given by

$$g_1(\tau) = \frac{< E_s(t)E_s^*(t+\tau) >}{< E_s(t)E_s^*(t) >}$$

Where, $E_s(t)$ is the sacttered intensity at time 't' and $E_s^*(t+\tau)$ is the scattered intensity at a time 't' plus a delayed time 'τ'

However in experiments one can only measure the intensity but not field. The normalized intensity-intensity autocorrelation function $g_2(\tau)$ is given by-

$$g_2(\tau) = \frac{< I_s(t)I_s^*(t+\tau) >}{< I_s(t)I_s^*(t) >}$$

For Gaussian wave, the field and intensity correlation function $g_1(\tau)$ and $g_2(\tau)$ are related through Siegert equation, given by:

$$g_2(\tau) = 1 + \beta|g_1(\tau)|^2$$

where β is the coherence factor.

So, $g_1(\tau)$ can be found from the above relation and $g_1(\tau)$ is related with decay constant Γ for a system under going Brownian motion by:

$$g_1(\tau) = e^{(-\Gamma\tau)}$$

where, Γ is given by: $\Gamma=Dq^2$

where D is the diffusion coefficient and q is the scattering vector. The magnitude of scattering wave vector is given by:

$$q = \left(\frac{4\pi n}{\lambda}\right)\sin\left(\frac{\theta}{2}\right)$$

where n = refractive index of medium, λ = wavelength of light in vacuum, θ = scattering angle.

The hydrodynamic radius R_H can be calculated using the Stoke-Einstein relation

$$D = (k_B T/6\pi\eta R_H)$$

Where k_B is Boltzmann constant, T is absolute temperature, η is viscosity and R_H is hydrodynamic radius (size of the particle).

The schematic and the photograph of the DLS set up is given in the figure below.

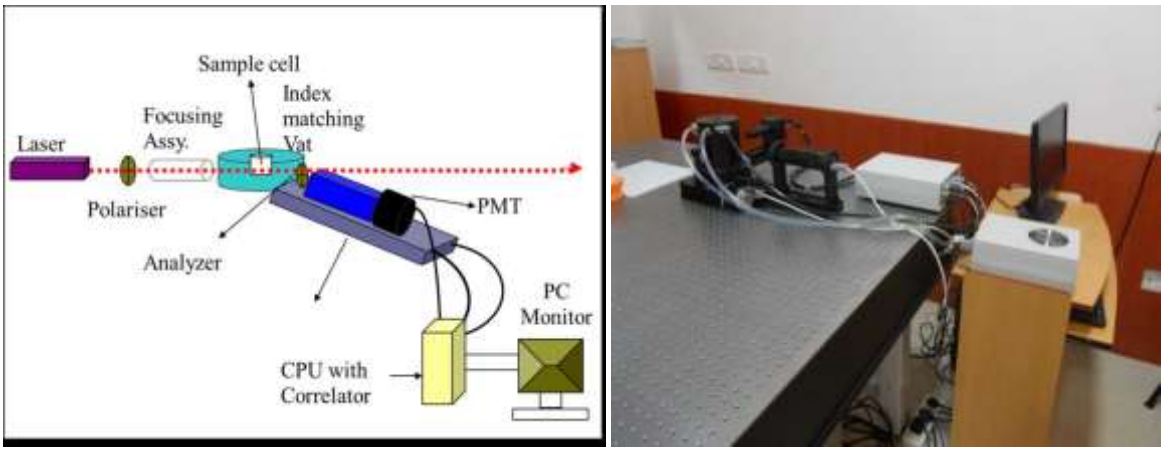

Fig 1: a) Schematic and b) Photograph of the DLS set up

2.2 Viscosity measurement

Viscosity of a polyelectrolyte solution varies with its conformation. In the absence of salt polyelectrolyte chains remain stretched due to the electrostatic repulsion between the like charges on the backbone. In this case the viscosity of the solution is more. However with increasing salt concentration the electrostatic repulsion gets screened and the polyelectrolytes started collapsing in turn viscosity gets reduced.

1ml solution is filled into the viscometer through its left arm. Then by creating suction at the tip of the other (right) arm the liquid is made to rise through the capillary in the right arm of the U-tube till it reaches above the mark 'A' as indicated in the figure below. The suction is then removed and the liquid is allowed to fall under its own weight. The time taken by the liquid to reach to the mark 'B' is noted down. This time is known as Efflux time.

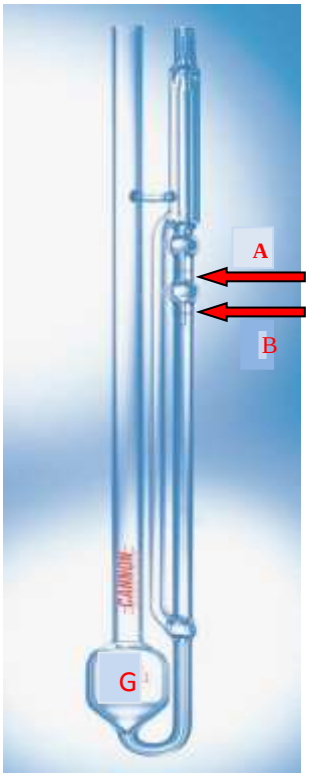

Fig 2: Cannon – Ubbelohde Viscometer

This viscometer has a viscometer constant 'k'. So, the viscosity can be measured from the following formula:

$$\eta = Efflux\ time * Viscometer\ constant$$

The efflux time for each sample was measured thrice and the average of the measurements was taken for the viscosity calculation.

CHAPTER – III

MATERIALS AND METHODS

3.1 Sample preparation for viscosity measurements:

Initially the buffer solution of pH 7 was prepared using Na_2HPO_4 and NaH_2PO_4. The prepared buffer solution was filtered using 0.22 μm membrane filter. Appropriate amount of sodium chloride was weighed and added to the buffer solutions to prepare 2M stock solution of NaCl. The salt solution was then diluted from the prepared stock solution using the buffer to desired concentrations of 500mM, 200mM, 100mM, and 10mM. To prepare the NaPSS solutions the required amount of NaPSS was weighed and added to the respective salt solutions. The NaPSS sample without any added salt was prepared separately. The samples were left overnight to allow the samples to dissolve properly in the salt solution. The samples were then mixed thoroughly in a vortex mixer. The prepared samples were then used for viscosity measurements in the Cannon – Ubbelohde viscometers.

3.2 Sample Preparation for DLS measurements:

The samples for DLS measurements have to be clean to avoid ambiguity in the results due to scattering from the dust particles, so extra care was taken to prepare the samples for the DLS measurements. The buffer solutions prepared was filtered and appropriate amount of NaCl was weighed and added to the filtered buffer solution. The salt solution was then centrifuged to remove any large particles in it. The stock solution was then diluted using the filtered buffer solutions to required salt concentrations of 500mM, 200mM, 100mM, and 10mM. Then required amount of NaPSS was then added to respective salt solutions. The prepared samples were then centrifuged for removal of dust and any large particles that might interfere with the measurements. The supernatant of each of the centrifuged sample was then transferred to clean sample cells for DLS measurements. The samples without any added salt was prepared separately and centrifuged before the DLS measurements were carried on it.

CHAPTER - IV

RESULTS AND DISCUSSION

4.1 Viscosity Measurements:

The viscosity variation with the salt concentration for sodium sulfonated polystyrene solutions is shown in the figure below. It is clearly seen from the figure that the solution viscosity decreases on increasing the electrolyte concentration.

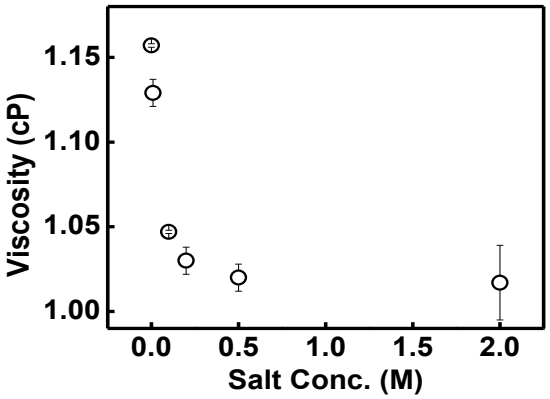

Fig 3: Viscosity versus salt concentration

The charges on the polyelectrolyte chains are increasingly screened by the counterions with the increase in salt concentration. This screening effect leads to the decrease in the strength of the electrostatic repulsion between the backbone charges and hence the chains assume a collapsed state in contrast to the extended state at zero salt concentration. The reduction in chain dimensions decreases the solution viscosity.

4.2 Dynamic Light Scattering measurements:

The autocorrelation function (ACF) against time and the particle size distribution for the NaPSS samples in 2M NaCl solutions is shown in the figure below.

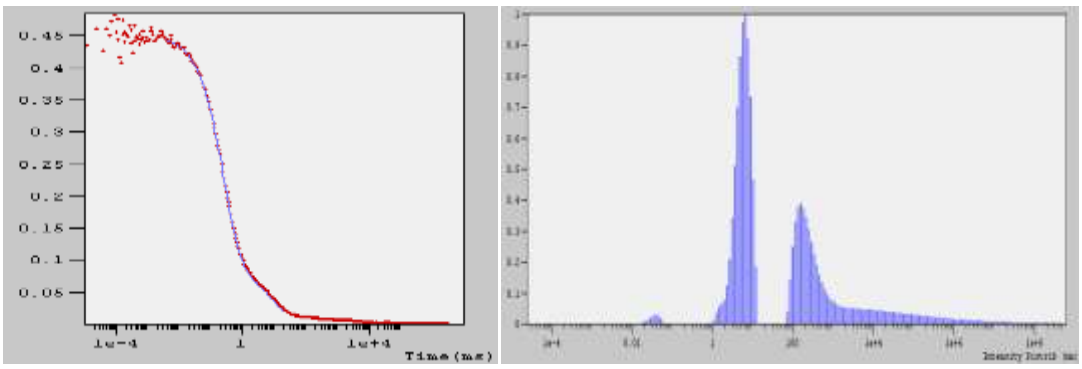

Fig 4: Autocorrelation function and Particle size distribution of NaPSS sample with 2M added salt

The particle size obtained for the NaPSS in 2M salt solution is found to be ~ 6nm. The particle size of NaPSS in 500mM and 200mM remains more or less same as that in the 2M solutions. However on decreasing the salt concentration the particle size increased.

The ACF against time and particle size distribution for the NaPSS samples in the 100mM salt is shown in the figure below.

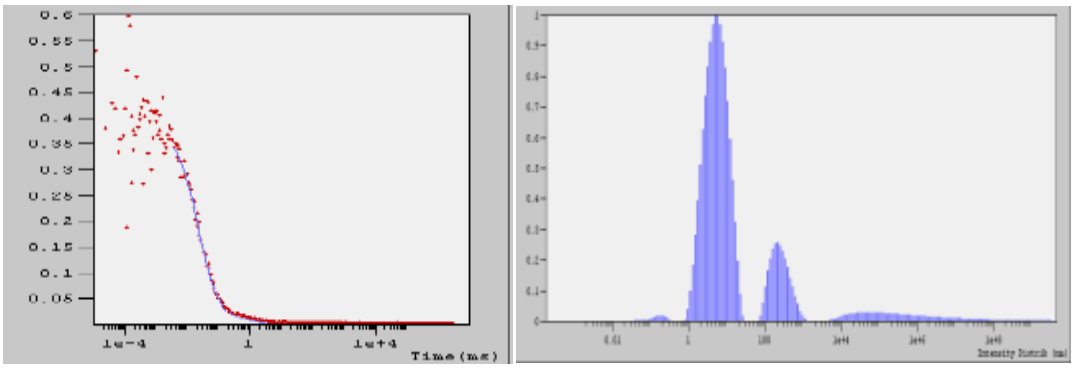

Fig 5: Autocorrelation function and Particle size distribution of NaPSS sample with 100mM added salt

The following figure shows the hydrodynamic radius of the particles against the salt concentration. It is found that the particle size decreases with the increase in salt concentration. As discussed earlier the screening of the backbone charges due to the counterions released from the salt is responsible for the reduction in the particle size from extended to coil state.

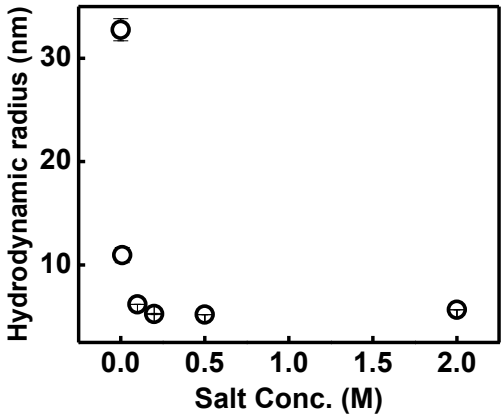

Fig 6: Hydrodynamic radius versus salt concentration

The results obtained from the experiments have been summarized in the table below.

Tabulation 1: Summary of Viscosity and DLS measurements

Salt Concentration (in M)	**Hydrodynamic radius (in nm)**	**Viscosity (cP)**
2.0	5.66±0.004	1.017±0.022
0.5	5.19±0.003	1.020±0.008
0.2	5.25±0.056	1.030±0.008
0.1	6.18±0.004	1.047±0.001
0.01	10.95±0.735	1.129±0.008
0	32.75±1.07	1.157±0.001

CHAPTER - V

CONCLUSIONS

The particle size obtained from the DLS measurements shows a reduction in the particle size of Sodium Sulfonated Polystyrene of molecular weight 70kDa from ~ 33 nm to ~ 6 nm on increasing the added electrolyte, NaCl concentration from 0M to 2M. The screening of the backbone charges due to the excess of counterions from the salt leads to the collapse of the polymer chains. The viscosity measurement also affirms this result which shows a decrease in the solution viscosity with the increasing salt concentration.

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